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(54) Title: RADIATION ACTIVATED HYDROSILATION REACTION

(57) Abstract

Numerous patents teach the use of various complexes of cobalt, rhodium, nickel, palladium, or platinum as catalysts for accelerating the thermally-activated addition reaction (hydrosilation) between a compound containing silicon-bonded hydrogen and a compound containing aliphatic unsaturation. Although platinum complexes and many others are useful as catalysts in processes for accelerating the thermally-activated addition reaction between compounds containing silicon-bonded hydrogen and compounds containing aliphatic unsaturation, processes for promoting the ultraviolet or visible radiation-activated addition reaction between these compounds are much less common. This invention provides a process for the addition reaction of compounds containing silicon-bonded hydrogen with compounds containing aliphatic unsaturation and compositions suitable for said process. The process is activated by actinic radiation and is conducted in the presence of a platinum complex having one diolefin group that is *eta*-bonded to the platinum atom and two aryl groups that are *sigma*-bonded to the platinum atom and a sensitizer that is capable of absorbing actinic radiation and is capable of transferring energy to said platinum complex such that the hydrosilation reaction is initiated upon exposure to actinic radiation. The invention also provides compositions for use in the aforementioned process.

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RADIATION ACTIVATED HYDROSILATION REACTIONBackground of the Invention1. Field of the Invention

10 This invention relates to a hydrosilation process involving the reaction of a compound containing silicon-bonded hydrogen with a compound containing aliphatic unsaturation in the presence of ultraviolet or visible radiation, and to compositions that are useful
15 in said process. The invention further relates to polysiloxane compositions, prepared by said process, which compositions are useful for preparing dental impressions, adhesives, release liners, and caulking materials.

20

2. Discussion of the Art

Numerous patents teach the use of various complexes of cobalt, rhodium, nickel, palladium, or platinum as catalysts for accelerating the
25 thermally-activated addition reaction (hydrosilation) between a compound containing silicon-bonded hydrogen and a compound containing aliphatic unsaturation. For example, U.S. Patent No. 4,288,345 (Ashby et al) discloses as a catalyst for hydrosilation reactions a
30 platinum-siloxane complex. U.S. Patent No. 3,470,225 (Knorre et al) discloses production of organic silicon compounds by addition of a compound containing silicon-bonded hydrogen to organic compounds containing at least one non-aromatic double or triple
35 carbon-to-carbon bond using a platinum compound of the empirical formula $PtX_2(RCOCR'COR'')$, wherein X is halogen, R is alkyl, R' is hydrogen or alkyl, and R'' is alkyl or alkoxy. The catalysts disclosed in the

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foregoing patents are characterized by their high catalytic activity. Other platinum complexes for accelerating the aforementioned thermally-activated addition reaction include: a platinacyclobutane complex having the formula $(PtCl_2-C_3H_6)_2$ (U.S. Patent No. 3,159,662, Ashby); a complex of a platinous salt and an olefin (U.S. Patent No. 3,178,464, Pierpoint); a platinum-containing complex prepared by reacting chloroplatinic acid with an alcohol, ether, aldehyde, or mixtures thereof (U.S. Patent No. 3,220,972, Lamoreaux); a platinum compound selected from trimethylplatinum iodide and hexamethyldiplatinum (U.S. Patent No. 3,313,773, Lamoreaux); a hydrocarbyl or halohydrocarbyl nitrile-platinum (II) halide complex (U.S. Patent No. 3,410,886, Joy); a hexamethyl-dipyridine-diplatinum iodide (U.S. Patent No. 3,567,755, Seyfried et al); a platinum curing catalyst obtained from the reaction of chloroplatinic acid and a ketone having up to 15 carbon atoms (U.S. Patent No. 3,814,731, Nitzsche et al); a platinum compound having the general formula $(R')PtX_2$, where R' is a cyclic hydrocarbon radical or substituted cyclic hydrocarbon radical having two aliphatic carbon-carbon double bonds, and X is a halogen or alkyl radical (U.S. Patent No. 4,276,252, Kreis et al); platinum alkyne complexes (U.S. Patent No. 4,603,215, Chandra et al.); platinum alkenylcyclohexene complexes (U.S. Patent No. 4,699,813, Cavezzan); and a colloidal hydrosilation catalyst provided by the reaction between a silicon hydride or a siloxane hydride and a platinum (0) or platinum (II) complex (U.S. Patent No. 4,705,765, Lewis). Although these platinum complexes and many others are useful as catalysts in processes for accelerating the thermally-activated addition reaction between the compounds containing silicon-bonded hydrogen and compounds containing aliphatic unsaturation, processes for promoting the ultraviolet or visible radiation-activated addition reaction between these

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compounds are much less common. Platinum complexes that can be used to initiate ultraviolet radiation-activated hydrosilation reactions have been disclosed, e.g.,
5 platinum azo complexes (U.S. Patent No. 4,670,531, Eckberg); (η^4 -cyclooctadiene)diarylplatinum complexes (U.S. Patent No. 4,530,879, Drahnak); and (η^5 -cyclopentadienyl)-trialkylplatinum complexes (U.S. Patent No. 4,510,094, Drahnak). Other compositions that
10 are curable by ultraviolet radiation include those described in U.S. Patent Nos. 4,640,939 and 4,712,092 and in European Patent Application No. 0238033. However, these patents do not indicate that the platinum complexes disclosed therein would be useful for
15 initiating the visible radiation-activated hydrosilation reaction. U.S. Patent No. 4,916,169 describes hydrosilation reactions activated by visible radiation.

Summary of the Invention

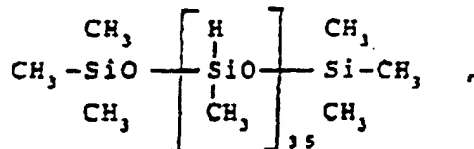
20 In one aspect, this invention provides an improved process for the actinic radiation-activated addition reaction of a compound containing silicon-bonded hydrogen with a compound containing aliphatic unsaturation, said addition being referred to
25 as hydrosilation, the improvement comprising using, as a platinum hydrosilation catalyst, an (η -diolefin)(σ -aryl)platinum complex, and, as a sensitizer, a compound that absorbs actinic radiation, i.e., light having a wavelength ranging from about 200
30 nm to about 800 nm and that is capable of transferring energy to the aforementioned platinum complex such that the hydrosilation reaction is initiated upon exposure to actinic radiation. The process is applicable both to the synthesis of low molecular weight compounds and to
35 the curing of high molecular weight compounds, i.e., polymers, containing unsaturated groups, e.g., $-C=C-$. For example, the process comprises exposing to actinic radiation, i.e., radiation having a wavelength of about

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200 nm to about 800 nm, a composition capable of undergoing hydrosilation comprising:

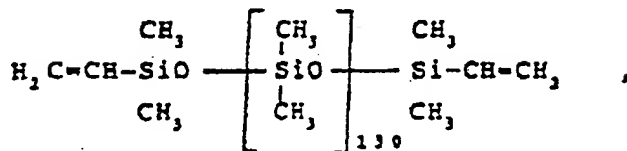
(a)

5



10

(b)



15

(c) a (η -diolefin)(σ -aryl)platinum complex catalyst, such as

(η^4 -1,5-cyclooctadiene)Pt(p-C₆H₄CH₃)₂, and

(d) a sensitizer capable of absorbing actinic radiation having a wavelength of about 200 nm to about 800 nm, and having a triplet energy of at least 31 Kcal/mole.

20

The invention further involves novel compositions, capable of undergoing hydrosilation, containing both the
25 the aforementioned platinum complex and the aforementioned sensitizer.

An important application of the process and compositions of the invention is as a visible light curable impression material for dental applications.

30

Advantages of the platinum complex and sensitizer in accelerating the actinic radiation-activated addition reaction of compounds containing silicon-bonded hydrogen with compounds containing aliphatic unsaturation include the following:

35

(1) the reaction composition will not react prematurely or readily in the absence of actinic radiation;

(2) since heat is not required, the addition

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reaction can be carried out on the surface of a heat-sensitive substrate without adversely affecting the substrate; and

- 5 (3) actinic radiation curing requires less energy than does thermal curing.

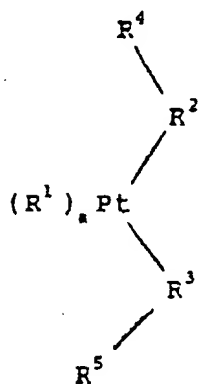
Detailed Description

As used in this application, the term
10 "compound", unless indicated otherwise, is a chemical substance which has a particular molecular identity or is made of a mixture of such substances, e.g., polymeric substances. The term "hydrosilation" means the addition
15 of organosilicon compounds containing silicon-bonded hydrogen to a compound containing an aliphatic multiple bond, and in the hydrosilation process described in this application, it refers to those processes in which platinum-containing catalysts are used to effect the
20 addition of an organosilicon compound having a silicon-bonded hydrogen atom to an aliphatically unsaturated compound having either olefinic or acetylenic unsaturation.

In a preferred embodiment of the invention, the platinum complex is an (η -diolefin)(σ -aryl)platinum
25 complex described in U.S. Patent No. 4,530,879, incorporated herein by reference, having the general structural formula:

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wherein

5 R^1 represents an alkadiene that is π -bonded to platinum, the alkadiene being a straight or branched chain group and preferably containing 4 to 12 carbon atoms, or a carbocyclic 6- to 8-membered ring preferably containing 6 to 12 carbon atoms, the alkadiene further being either
10 unsubstituted or substituted with one or more groups that are inert in a hydrosilation reaction;

15 R^2 and R^3 represent aryl radicals that are σ -bonded to platinum and are independently selected from monocyclic and polycyclic aryl radicals preferably containing 6 to 18 carbon atoms, said aryl radicals being either unsubstituted or substituted with
20 one or more groups that are inert in a hydrosilation reaction;

R^4 and R^5 each independently represents hydrogen, or an alkenyl radical preferably containing 2 to 6 carbon atoms in a
25 straight or branched chain, or a cycloalkenyl radical containing 5 or 6 ring carbon atoms, the unsaturated bond of the alkenyl or cycloalkenyl radical being in the 2- or 3-position with respect to the σ -bonded position; and
30

a represents zero or one, being zero only when both R^4 and R^5 are said alkenyl radicals and being one when either R^4 or R^5 is not said alkenyl radical.

35 Representative examples of suitable (η^4 -1,5-cyclooctadiene)diarylplatinum complexes are (COD)Pt(p -C₆H₄CH₃)₂ and (COD)Pt(p -C₆H₄OCH₃)₂, in which (COD) represents the (η^4 -1,5-cyclooctadiene) group.

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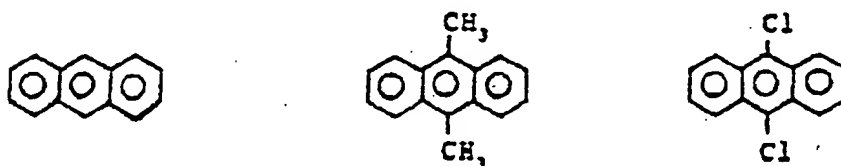
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Sensitizers suitable for this invention are those compounds capable of absorbing actinic radiation within the ultraviolet and visible regions of the electromagnetic spectrum, i.e., about 200 nm to about 800 nm, and capable of transferring energy to the platinum complex. It has been discovered that they must have a triplet energy level of at least 31 Kcal/mole, and must not inhibit the hydrosilation reaction.

Sensitizers are preferably selected from two classes of compounds: 1) polycyclic aromatic compounds, and 2) aromatic compounds containing a ketone chromophore. The sensitizer compounds can be substituted with any substituent that does not interfere with the light absorbing and energy transferring capabilities of the sensitizer compound or the hydrosilation catalyst. Examples of typical substituents include alkyl, alkoxy, aryl, aryloxy, aralkyl, alkaryl, halogen, etc. Representative examples of polycyclic aromatic sensitizers suitable for the invention include anthracene, 9-vinylanthracene, 9,10-dimethylantracene, 9,10-dichloroanthracene, 9,10-dibromoanthracene, 9,10-diethylantracene, 9,10-diethoxyanthracene, 2-ethyl-9,10-dimethylantracene, naphthacene, pentacene, benz[a]anthracene, 7,12-dimethylbenz[a]anthracene, azulene and the like.

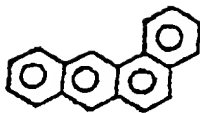
Some of the foregoing examples are illustrated below:

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35 anthracene 9,10-dimethylantracene 9,10-dichloroanthracene

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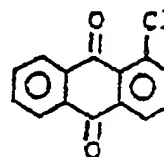
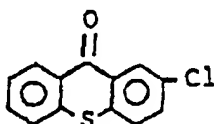
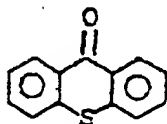
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benz[a]anthracene

Representative examples of aromatic ketone sensitizers suitable for this invention include

2-chlorothioxanthone, 2-isopropylthioxanthone, thioxanthone, anthraquinone, benzophenone, 1-chloroanthraquinone, bianthrone, and the like. Some of the foregoing examples are illustrated below:

15



20

thioxanthone 2-chlorothioxanthone 1-chloroanthraquinone

Turning now to the reactants to be used in the radiation-activated addition reaction, compounds containing aliphatic unsaturation which are useful in the present invention have olefinic or acetylenic unsaturation. These compounds are well-known in the art of hydrosilation and are disclosed in such patents as U.S. Patent No. 3,159,662 (Ashby), U.S. Patent No. 3,220,972 (Lamoreaux), and U.S. Patent No. 3,410,886 (Joy), which disclosures of said compounds are incorporated herein. In instances where these unsaturated compounds contain elements other than carbon and hydrogen, it is preferred that these elements be either oxygen, nitrogen, silicon, a halogen, or a combination thereof. The aliphatically unsaturated compound can contain one or more carbon-to-carbon multiple bonds. Representative examples of the aliphatically unsaturated hydrocarbons which can be

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employed include mono-olefins, for example, ethylene, propylene, and 2-pentene, diolefins, for example, divinylbenzene, butadiene, and 1,5-hexadiene, cycloolefins, for example, cyclohexene and cycloheptene, and monoalkynes, for example, acetylene, propyne, and 1-buten-3-yne. The aliphatically unsaturated compounds can have up to 20 to 30 carbon atoms, or more.

Oxygen-containing aliphatically unsaturated compounds can also be used, especially where the unsaturation is ethylenic, such as methyl vinyl ether, divinyl ether, phenyl vinyl ether, monoallyl ether of ethylene glycol, allyl aldehyde, methyl vinyl ketone, phenyl vinyl ketone, acrylic acid, methacrylic acid, methyl acrylate, allyl acrylate, methyl methacrylate, allyl methacrylate, vinylacetic acid, vinyl acetate, and linolenic acid. Heterocyclic compounds containing aliphatic unsaturation in the ring, such as dihydrofuran, and dihydropyran, are also suitable for the present invention.

Halogenated derivatives of the previously mentioned aliphatically unsaturated compounds can be employed, including acyl chlorides as well as compounds containing a halogen substituent on a carbon atom other than a carbonyl carbon atom. Such halogen-containing compounds include, for example, vinyl chloride, and the vinyl chlorophenyl esters.

Unsaturated compounds containing nitrogen substituents such as acrylonitrile, N-vinylpyrrolidone, alkyl cyanide, nitroethylene, etc., are also useful in the practice of the present invention.

Other unsaturated compounds useful in the practice of the present invention include polymers containing aliphatic unsaturation, such as the polyester resins prepared from polybasic saturated or unsaturated acids with polyhydric unsaturated alcohols, and the polyester resins prepared by reacting unsaturated polybasic acids with saturated polyhydric alcohols.

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A particularly useful type of unsaturated compound which can be employed in the practice of the present invention is that containing silicon, such as those compounds commonly referred to as organosilicon monomers or polymers. These unsaturated organosilicon compounds have at least one aliphatically unsaturated organic radical attached to silicon per molecule. The aliphatically unsaturated organosilicon compounds include silanes, polysilanes, siloxanes, silazanes, as well as monomeric or polymeric materials containing silicon atoms joined together by methylene or polymethylene groups or by phenylene groups.

Preferred among the aliphatically unsaturated organosilicon compounds useful in the present invention are the monomeric silanes having the empirical formula:



the cyclopoly siloxanes having the empirical formula:



and the polyorganosiloxanes having the empirical formula:



wherein

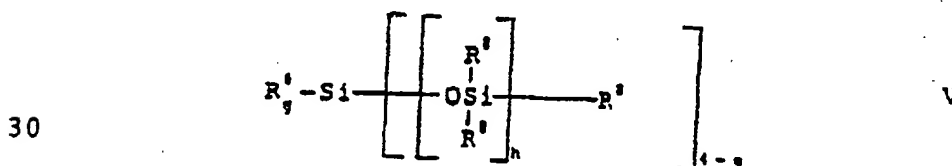
- 30 R^6 represents a monovalent aliphatic unsaturated hydrocarbyl group,
 R^7 represents a monovalent saturated hydrocarbyl group,
 X represents a hydrolyzable group,
 35 b represents an integer from 1 to 4, inclusive,
 c represents zero or an integer from 1 to 3, inclusive, the sum of b and c being 1 to 4,

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- d represents an integer from 3 to 18, inclusive,
 e represents a number having a value of 0.0001
 to 1, inclusive, and
 5 f represents zero or a number such that the sum
 of e and f is equal to 1 to 2, inclusive.

Monovalent aliphatic unsaturated hydrocarbyl
 groups represented by R^6 include alkenyl, for example,
 vinyl, propenyl, isopropenyl, 3-butenyl, and 5-hexenyl.
 10 Groups represented by R^7 include, for example, alkyl
 groups, such as methyl, ethyl, and pentyl; cycloalkyl
 groups, such as cyclopentyl and cyclohexyl; aryl groups
 such as phenyl and tolyl; aralkyl groups, such as benzyl
 and phenylethyl; and halogenated hydrocarbyl groups,
 15 such as haloalkyl, e.g., chloromethyl, trichloromethyl,
 and 3,3,3-trifluoropropyl, and haloaryl, e.g.,
 chlorophenyl. Hydrolyzable groups represented by X
 include, for example, halogen groups such as chloro,
 bromo, and iodo, alkoxy groups such as methoxy, ethoxy,
 20 and phenoxy, and acyloxy groups such as acetoxy,
 propionoxy, and benzoyloxy. A hydrolyzable group is one
 which undergoes a displacement reaction with water.

In one particularly preferred embodiment of
 the process of the invention, the compound containing
 25 aliphatic unsaturation is an aliphatically unsaturated
 polyorgano- siloxane represented by the general formula:



wherein

each R^8 can be the same or different and represents
 a non-halogenated or halogenated
 35 ethylenically- unsaturated group having from 2
 to 18 carbon atoms, such as vinyl, propenyl,
 and chlorovinyl, a non-halogenated or
 halogenated alkyl group having from 1 to 18

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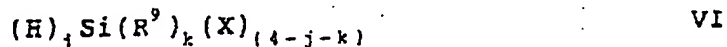
carbon atoms, such as methyl, thyl, propyl, hexyl, octyl, dodecyl, octadecyl, trichloromethyl, and 3,3,3-trifluoropropyl, a non-halogenated or halogenated cycloalkyl group having from 3 to 12 carbon atoms, such as cyclopentyl and cyclohexyl, or phenyl, at least 70% of all R^8 groups being methyl groups, but no more than 10% of all R^8 groups being vinyl or other alkenyl, e.g., having 3 to 18 carbon atoms, and at least one of the R^8 groups being vinyl or other alkenyl, e.g., having 3 to 18 carbon atoms,

h represents a number having a value from 1 to about 3,000,

g represents 0, 1, 2, or 3.

The reactant containing the silicon-hydrogen linkage can be a polymeric compound or a compound that is not polymeric. These compounds are well-known in the art and are disclosed in the patents which describe the aliphatically unsaturated reactant, i.e., Ashby, U.S. Patent No. 3,159,662; Lamoreaux, U.S. Patent No. 3,220,972; and Joy, U.S. Patent No. 3,410,886. The reactant containing the silicon-hydrogen linkage should contain at least one silicon-bonded hydrogen atom per molecule, with no more than three hydrogen atoms attached to any one silicon atom.

Some classes of compounds having a silicon-bonded hydrogen atom which can be used in the invention are organosilanes having the empirical formula:

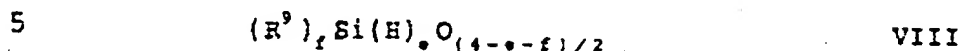


organocyclopolysiloxanes having the empirical formula:



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and organohydrosiloxane polymers or copolymers having the empirical formula:



wherein

- R^9 represents an organic group, preferably selected from the group consisting of monovalent hydrocarbyl groups, and halogenated monovalent hydrocarbyl groups,
- j represents the integer 1, 2, or 3,
- k represents zero or an integer of 1 to 3, inclusive, the sum of j and k being equal to 1 to 4, and

x , d , e and f are as defined above for formulas II, III, and IV.

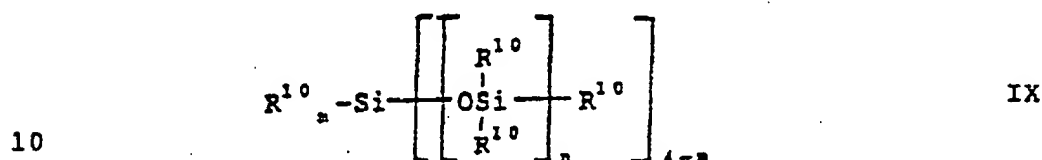
Among the groups represented by R^9 include, for example, alkyl groups having 1 to 18 carbon atoms, e.g., methyl, ethyl, propyl, octyl, and octadecyl, cycloalkyl groups having 5 to 7 ring carbon atoms, e.g., cyclohexyl and cycloheptyl, aryl groups having 6 to 18 carbon atoms, e.g., phenyl, naphthyl, tolyl, xylyl, and combinations of alkyl and aryl groups, e.g., aralkyl groups, such as, benzyl and phenylethyl, and halo-substituted groups thereof, e.g., chloromethyl, chlorophenyl, and dibromophenyl. Preferably, the R^9 group is methyl or both methyl and phenyl. The R^9 group can also be an unsaturated aliphatic group having 1 to 20 carbon atoms, such as alkenyl or cycloalkenyl, e.g., vinyl, allyl and cyclohexenyl. When the R^9 group is a group with aliphatic unsaturation, the silicon compound containing silicon-hydrogen linkages can be reacted with itself to form a polymer.

Among the inorganic compounds which contain silicon-bonded hydrogen atoms and which are useful as reactants in the process of the present invention are included, for example, trichlorosilane, dibromosilane,

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pentachlorodisilane, pentachlorodisiloxane, and heptachlorotrisilane.

A preferred compound having silicon-bonded hydrogen useful in this invention is a polyorganohydrosiloxane having the general formula:



wherein

each R^{10} can be the same or different and represents hydrogen, an alkyl group having 1 to 18 carbon atoms, a cycloalkyl group having 3 to 12 carbon atoms, or a phenyl group, at least one but not more than one-half of all the R^{10} groups in the siloxane being hydrogen, m represents 0, 1, 2, or 3, and n represents a number having an average value from 1 to about 3,000.

The hydrosilation composition useful in the synthesis of low molecular weight compounds by the process of the invention can be prepared by mixing about 0.1 to about 10.0 equivalent weights of the compound having silicon-bonded hydrogen with one equivalent weight of the compound having aliphatic unsaturation and then adding an amount of platinum complex catalyst sufficient to catalyze the reaction and an amount of sensitizer sufficient to sensitize the platinum complex upon exposure to actinic radiation having a wavelength from about 200 nm to about 800 nm. The amount of the catalyst can range from about 5 to about 1,000 parts by weight, preferably from about 50 to about 500 parts by weight, per 1,000,000 parts by weight of the total composition. The amount of sensitizer can range from about 50 to about 50,000 parts by weight, preferably from about 500 to about 5,000 parts by weight, per

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1,000,000 parts by weight of total composition.

Known techniques can be used to conduct the hydrosilation reaction. In carrying out a hydrosilation reaction in the practice of this invention, the reactants and catalyst can be introduced into a vessel equipped for stirring, where the mixture is stirred until it is homogenous. If either of the reactants is a solid or is extremely viscous, a solvent can be introduced into the vessel to facilitate uniform mixing of the reactants. Suitable solvents include aromatic hydrocarbons, such as xylene and toluene, aliphatic hydrocarbons, such as hexane and mineral spirits, and halogenated hydrocarbons, such as chlorobenzene and trichloroethane. It is desirable that the solvent be transmissive to actinic radiation. From about 0.1 to about 10 parts of solvent per part by weight of the combined reactants may be used. The resulting reaction product will generally be sufficiently pure for its intended use. However, it may be desirable to remove the solvent if one has been employed.

The hydrosilation compositions useful in the preparation of higher molecular weight cured siloxane polymers, by the process of this invention, can be prepared by mixing an aliphatically unsaturated polysiloxane and the compound having silicon-bonded hydrogen in such a proportion so as to provide about 0.1 to about 10.0 silicon-bonded hydrogen atoms per unsaturated group, and then adding from about 5 to about 1,000 parts by weight, preferably from about 50 to about 500 parts by weight of platinum complex catalyst and from about 50 to about 50,000 parts by weight, preferably from about 500 to about 5,000 parts by weight of sensitizer, per 1,000,000 parts by weight of the total composition. The reaction mixture can be mixed, as by stirring, blending, or tumbling, until it is homogenous.

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Th thoroughly mixed composition can then be applied to a substrate by any suitable means, such as by spraying, dipping, knife coating, curtain coating, roll coating, or the like, and the coating cured by using conventional techniques for providing actinic radiation. It is preferred that curing be conducted by exposing the coated substrate to radiation having a wavelength of about 200 nm to about 800 nm. Depending on the particular silicone formulation, catalyst, sensitizer and intensity of the actinic radiation, curing can be accomplished in a period from less than one second to less than 30 minutes. Any radiation source emitting radiation above about 200 nm can be used. Examples of suitable radiation sources include tungsten halogen lamps, xenon arc lamps, mercury arc lamps, incandescent lamps, and fluorescent lamps. Particularly preferred sources of visible radiation are tungsten halogen, xenon arc, and mercury arc lamps.

Various additives conventionally included in hydrosilation compositions can be included in the curable compositions, depending on the intended purpose of the composition. Fillers and/or pigments, such as chopped fibers, crushed polymers, talc, clay, titanium dioxide, and fumed silica can be added. Soluble dyes, oxidation inhibitors, and/or any material that does not interfere with the catalytic activity of the platinum complex and does not absorb actinic radiation at the absorption wavelength of the sensitizer can be added to the composition.

The shelf life of the curable compositions containing the catalyst and sensitizer can be extended by the addition of a conventional catalyst inhibitor. The amount of catalyst inhibitor can vary from about 1 to about 10 times, or more, the amount of platinum complex, depending on the activity of the particular complex or complex-accelerator used and the shelf life desired for the composition. Greater amounts of

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inhibitor should be used with the more active complexes, with lesser amounts being used for the less active complexes. Hydrosilation inhibitors are well known in the art and include such compounds as acetylenic alcohols, certain polyolefinic siloxanes, pyridine, acrylonitrile, organic phosphines and phosphites, unsaturated amides, and alkyl maleates.

The hydrosilation compositions of this invention can be applied to the surface of any solid substrate for a variety of purposes. Examples of such substrates include paper, cardboard, wood, cork, plastic, such as polyester, nylon, polycarbonate, etc., woven and nonwoven fabric, such as cotton, polyester, nylon, etc., metal, glass, and ceramic.

It is often advantageous to prime the surface of non-porous substrates to which the hydrosilation composition is to be applied to improve the adhesion of the composition to the substrate. Many primers and priming techniques (e.g., corona treatment) are described in the art and should be chosen on the basis of the substrate to be used. For example, the epoxy-functional siloxanes as taught in U.S. Patent No. 4,243,718 (Murai, et al) are useful for priming the surface of plastic films such as polyester and polyvinylchloride.

Compositions of this invention can be applied and cured in relatively thick sections, such as an impression material for dental applications or a fast-setting caulking material.

Advantages of this invention are further illustrated by the following examples, where the parts referred to are parts by weight. The particular materials and amounts recited as well as other conditions and details given should not be construed to unduly limit this invention.

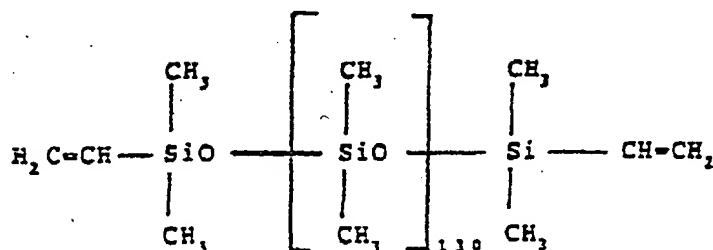
Compositions of this invention were evaluated for cure speed in the following manner.

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Molds made from a 1.5 mm thick "Teflon" sheet with a 6 mm diameter hole through the sheet were clamped to clean glass slides so that the central axis of the hole in the mold was normal to the glass slide. The hole was filled with a sample of the composition being evaluated. A "Visilux" 2 dental curing light (available from Minnesota Mining and Manufacturing Company, St. Paul, Minnesota) with a light output in the visible region of the spectrum between 400 and 500 nm was clamped to a ring stand and positioned such that the cylindrical tip of the light source was 5.0 mm above the top of the "Teflon" mold. The center of the 6 mm diameter sample was directly beneath the light tip. The sample was irradiated with the "Visilux" 2 light until a tack-free, cohesive silicone polymer was obtained as determined with a metal probe. In order to evaluate compositions for cure speed upon exposure to ultraviolet radiation, small samples of each formulation were placed in shallow 2-inch diameter aluminum pans and irradiated at a distance of 25 cm under a bank of six Sylvania 15-watt "Black Light" bulbs having a maximum intensity output at 365 nm. All samples were tested in duplicate or triplicate.

Example 1

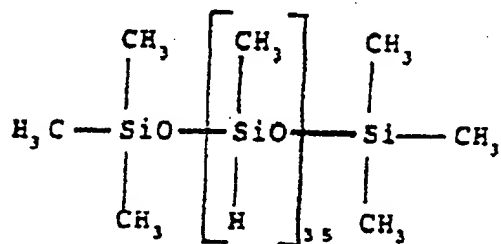
A stock composition was prepared by mixing in a glass container 97.5 parts by weight of vinyl terminated polydimethylsiloxane polymer having the formula:



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and 2.5 parts by weight of a compound containing silicon-bonded hydrogen having the formula:



To 10.0 g aliquots of this composition were added a photohydrosilation catalyst at a concentration of 200 ppm Pt selected from $(\text{COD})\text{Pt}(\text{m-C}_6\text{H}_4\text{CF}_3)_2$, $(\text{COD})\text{Pt}(\text{p-C}_6\text{H}_4\text{SiMe}_3)_2$, $(\text{COD})\text{Pt}(\text{p-C}_6\text{H}_4\text{Me})_2$, and $(\text{COD})\text{Pt}(\text{p-C}_6\text{H}_4\text{OMe})_2$ and one of the photosensitizers listed in Table I at a concentration of 500 ppm.

Samples were irradiated as previously described, and the time until gelation of these compositions is set forth in Table I.

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Table I

5	Aryl group of catalyst	Sensitizer	Gel time (sec)	
			"Black Light"	"Visilux" 2
	m-C ₆ H ₄ CF ₃	--	300	180
	m-C ₆ H ₄ CF ₃	2-chlorothioxanthone	390	300
10	m-C ₆ H ₄ CF ₃	9,10-dimethylantracene	480	210
	p-C ₆ H ₄ Si(CH ₃) ₃	--	330	140
	p-C ₆ H ₄ Si(CH ₃) ₃	2-chlorothioxanthone	390	140
	p-C ₆ H ₄ Si(CH ₃) ₃	9,10-dimethylantracene	420	180
	p-C ₆ H ₄ CH ₃	--	480	240
15	p-C ₆ H ₄ CH ₃	2-chlorothioxanthone	480	120
	p-C ₆ H ₄ CH ₃	9,10-dimethylantracene	570	205
	p-C ₆ H ₄ OCH ₃	--	530	480
	p-C ₆ H ₄ OCH ₃	2-chlorothioxanthone	172	25
	p-C ₆ H ₄ OCH ₃	2-isopropylthioxanthone	345	48
20	p-C ₆ H ₄ OCH ₃	9,10-dimethylantracene	570	467
	p-C ₆ H ₄ OCH ₃	9,10-dichloroanthracene	320	87
	p-C ₆ H ₄ OCH ₃	9-vinylnanthracene	750	330
	p-C ₆ H ₄ OCH ₃	2,7-dichloro-9-fluorenone	555	76
	p-C ₆ H ₄ OCH ₃	4-chlorobenzophenone	390	300
25	p-C ₆ H ₄ OCH ₃	camphorquinone	480	90
	p-C ₆ H ₄ OCH ₃	azulene	660	430

The data in Table I indicate that several photosensitizers are capable of increasing the cure speed of this silicone formulation; of the photosensitizers examined, 2-chlorothioxanthone provided the greatest degree of increase in cure speed. The results also suggest that (COD)PtAr₂ complexes bearing electron-rich aryl groups are more readily accelerated by photosensitizers than are derivatives bearing electron-poor aryl groups.

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Example 2

To 10.0 g aliquots of the composition of Example 1 were added the photohydrosilation catalyst (COD)Pt(p-C₆H₄OCH₃)₂ at a concentration of 200 ppm Pt and varying amounts of the photosensitizer 2-chlororothioxanthone. Samples were irradiated as previously described, and the time until gelation of these compositions is set forth in Table II.

Table II

Amount of sensitizer (ppm)	Gel time (sec)	
	"Black Light"	"Visilux" 2
15		
-	560	450
50	360	60
100	290	33
200	240	25
20		
500	170	19
1000	180	16
2000	165	15

The data in Table II indicate that when using the catalyst (COD)Pt(p-C₆H₄OCH₃)₂, the rate of cure increases with increasing amounts of 2-chlororothioxanthone under a "Black Light" source (<400 nm) up to a level of at least 2,000 ppm and under a "Visilux" 2 source (400-500 nm) up to a level of about 1,000 ppm.

Example 3

This example illustrates the release characteristics of coatings prepared with the compositions of this invention. To a 30.0 g aliquot of the stock composition of Example 1 were added 15.8 mg of (COD)Pt(p-C₆H₄OCH₃)₂ (200 ppm Pt) and 15 mg of

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2-chlorothioxanthone (500 ppm). The composition was coated on super calendered Kraft paper at a coating weight of 1 to 2 g/m² and cured by irradiation under an atmosphere of nitrogen in a PPG processor that advanced the sample at a rate of 50 cm/sec under two medium pressure mercury lamps emitting 120 watts of radiation per centimeter of lamp length and subsequent heating in a circulating air oven at 100°C for 2 minutes. Similarly coated samples that were not exposed to radiation did not cure when heated at 100°C.

The release value of the cured silicone coating was determined by the following procedure: A heptane-isopropyl alcohol solution of pressure-sensitive adhesive comprising isooctyl acrylate (95.5% by weight)-acrylic acid (4.5% by weight) copolymer, as described in Example 5 of U.S. Patent No. Re. 24,906, incorporated herein by reference, was applied to the cured silicone coating and dried for 5 minutes at 70°C in a circulating air oven to give a dry coating weight of 32 g/m². A biaxially oriented film of polyethylene terephthalate (PET) (38 micrometers thick) was pressed against the surface of the coating to produce a laminate consisting of a pressure-sensitive adhesive tape and a silicone-coated substrate. The laminate was cut into 2.5 x 25 cm strips. An average value of 15 g per 2.5 cm of width was measured to be the force required to pull the PET film with adhesive attached thereto (i.e., a pressure-sensitive adhesive tape) away from the silicone-coated substrate at an angle of 180° and a pulling speed of 230 cm/min.

The readhesion value of the pressure-sensitive tapes was determined by the following procedure: The pressure-sensitive tapes, as removed from the silicone coated surface, were applied to the surface of a clean glass plate. An average value of 1,400 g per 2.5 cm of width was measured to be the force required to pull the tape from the glass surface at an angle of 180° and a

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pulling speed of 230 cm/min. A control readhesion value was obtained for the pressure-sensitive tape by applying the tape, which had not been placed in contact with a
5 silicone-coated surface, to a clean glass plate and measuring the force required to remove the tape from the plate. The control readhesion value was 1,500 g per 2.5 cm of width.

10

Example 4

This example illustrates the preparation of a silicone-based pressure-sensitive adhesive tape from a composition of this invention. A mixture of the following three ingredients was prepared:

15

- (1) 13.6 g of a dimethylvinylsiloxane endblocked polydimethylsiloxane containing an average of 25.1 dimethylsiloxane units per molecule;
- 20 (2) 25.6 g of a dimethylhydrogensiloxane endblocked polydimethylsiloxane containing an average of 28.7 dimethylsiloxane units per molecule; and
- (3) 100.0 g of a 60 percent by weight solution in xylene of a resinous organosiloxane copolymer comprising $\text{CH}_3\text{SiO}_{1/2}$, $\text{SiO}_{3/2}\text{H}$ and $\text{SiO}_{4/2}$ units in a ratio of 41.6 : 10.5 : 47.6. The
25 copolymer exhibited a number average molecular weight, determined by gel permeation chromatography, of about 2,600 and a dispersity index of 2.6.

30

The mixture was stripped of volatile material by heating at 65°C under less than 0.5 mm of Hg pressure on a rotary evaporator. To the resulting viscous
35 mixture were added 0.80 g of 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane, 2.0 g of toluene, 131 mg of (COD)Pt(p-C₆H₄OCH₃)₂ (500 ppm Pt) and 100 mg of 2-chlorothioxanthone (1,000 ppm). The composition was

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knife coated at a thickness of 0.05 mm on a 0.05 mm thick polyethylene terephthalate film, and the coating was cured by irradiation under an atmosphere of nitrogen in a PPG processor that advanced the sample at a rate of 50 cm/sec under two medium pressure mercury lamps emitting 120 watts of radiation per centimeter of lamp length and subsequent heating in a circulating air oven at 100°C for two minutes.

Adhesion was determined essentially according to the procedure described in ASTM D-330 (1983). Strips of the tape 2.54 cm wide and approximately 25 cm long were adhered to a glass surface using a 2.04 kg rolled weight. An average value of 1,600 g per 2.5 cm of width was measured to be the force required to pull the adhesive tape away from the glass surface at an angle of 180° and a pulling speed of 230 cm/min.

Shear strength was determined essentially according to the procedure described in ASTM D-3654 (1982). Specimens 1.27 cm wide and approximately 8 cm long were adhered to a bright annealed steel surface with an overlap area of 1.27 cm by 1.27 cm. The samples were suspended vertically and maintained at a temperature of 70°C for one hour. A 1 kg weight was suspended from the free end of each specimen, and an average of 200 minutes was measured as the elapsed time before the adhesive bond failed while being maintained at a temperature of 70°C. The test was repeated at room temperature, and an average holding time exceeding 10,000 minutes was measured.

The tack of the adhesive tape was measured qualitatively by touching the cured adhesive with a finger. Tack was judged to be moderate.

35

Example 5

This example illustrates the preparation of a conformal coating for electronic components using a

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composition of this invention. A composition consisting of the following ingredients in the amounts indicated was prepared:

5		
	Ingredient	Amount (parts by weight)
	Vinyl siloxane polymer ¹	54.2
10	Crosslinking Agent ²	30.8
	(COD)Pt(p-C ₆ H ₄ OCH ₃) ₂	0.053
	Sensitizer (2-chlorothioxanthone)	0.050
	Fumed silica ³	15.0
15	¹ CH ₂ =CH-Si(CH ₃) ₂ -[OSi(CH ₃) ₂] ₁₃₀ -CH=CH ₂	
	² PMC 54, available from Minnesota Mining and Manufacturing Company	
	³ "Quso", available from Degussa Corporation	

20 The ingredients were introduced into a 250 ml beaker and mixed thoroughly. The mixture was transferred to a 50 cc syringe and degassed under reduced pressure for approximately 30 minutes to yield a bubble-free mixture.

25 The composition was applied to an integrated circuit board measuring 2 inches by 2 inches in sufficient quantity to provide a coating approximately 1 mm in thickness. The coating was irradiated with a "Visilux" 2 light source for approximately 4 minutes to provide a tough, elastomeric, transparent coating that adhered well to the circuit board.

Example 6

35 This example illustrates preparation of a dental impression by means of a visible-light curable wash material and a chemically curable tray material.

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A polyvinylsiloxane formulation curable by visible light was prepared by mixing the following ingredients in the amounts indicated:

5

		<u>Amount</u>	
<u>Ingredient</u>		<u>(g)</u>	<u>(wt %)</u>
Vinyl-terminated polysiloxane			
polymer ¹		8.5	76.81
10	Crosslinking agent ²	1.5	13.56
	(COD)Pt(p-C ₆ H ₄ OCH ₃) ₂	0.015	0.14
	Sensitizer (2-chlorothioxanthone)	0.01	0.09
	Fumed silica ³	<u>1.0</u>	<u>9.04</u>
		11.065	100.00
15	¹ $\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_2-\text{[OSi}(\text{CH}_3)_2\text{]}_{300}-\text{CH}=\text{CH}_2$		
	² PMC 54, available from Minnesota Mining and Manufacturing Company		
	³ "Quso", available from Degussa Corporation		

- 20 The first four ingredients were premixed; then fumed silica was added. The resultant mixture was painted on the entire surface of a single tooth of a typodont. The coated surface was then irradiated by means of a "Visilux" 2 light over the entire surface for
- 25 approximately two minutes or until the resin was completely tack-free. Immediately following the irradiation step, a two-part chemically curable impression material (Express Medium Viscosity Wash, Minnesota Mining and Manufacturing Company, St. Paul,
- 30 Minnesota) was applied by syringe directly over the several teeth both adjacent to and including those previously irradiated with light. The material was allowed to set for about five minutes. The bulk material was easily removed from the typodont by firmly
- 35 holding the typodont in one hand and the impression in the other. Upon removal of the silicone impression, it was observed that the light-cured material was firmly and completely bonded to the chemically-cured material.

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The stone model that was prepared from the impression showed improved detail where the light cured material was placed.

5

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this
10 invention is not to be unduly limited to the illustrated embodiments set forth herein.

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WHAT IS CLAIMED IS:

1. A hydrosilation process which comprises
5 reacting a composition comprising a compound having aliphatic unsaturation and a compound containing at least one silicon-bonded hydrogen atom and not having more than three hydrogen atoms attached to any one silicon atom, in the presence of both a
10 (η -diolefin)(σ -aryl)platinum complex and a sensitizer that is capable of absorbing actinic radiation and that is capable of transferring energy to said platinum complex such that the hydrosilation reaction is initiated upon exposure to actinic radiation.
15
2. The process of Claim 1, wherein said reaction is carried out by means of exposing said composition to actinic radiation.
- 20 3. The process of Claim 1, wherein said sensitizer has a triplet energy of at least 31 Kcal/mole.
- 25 4. The process of Claim 1, wherein said sensitizer is a polycyclic aromatic compound.
5. The process of Claim 4, wherein said polycyclic aromatic compound has from two to five rings, inclusive.
30
6. The process of Claim 5, wherein said polycyclic aromatic compound is selected from the group consisting of 9,10-dimethylantracene, 9,10-dichloroanthracene, and azulene.
35
7. The process of Claim 1, wherein said sensitizer is an aromatic compound containing a ketone chromophore.

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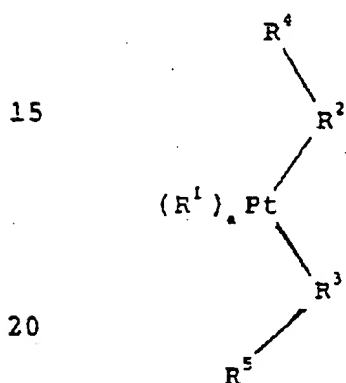
8. The process of Claim 7, wherein said aromatic compound is a thioxanthone.

5

9. The process of Claim 8, wherein said thioxanthone is selected from the group consisting of 2-chlorothioxanthone and 2-isopropylthioxanthone.

10

10. The process of Claim 1, wherein the platinum complex has the formula:



wherein

25

R^1 represents an alkadiene that is π -bonded to platinum, the alkadiene being a straight or branched chain group and preferably containing 4 to 12 carbon atoms, or a carbocyclic 6- to 8-membered ring preferably containing 6 to 12 carbon atoms, the alkadiene further being either unsubstituted or substituted with one or more groups that are inert in a hydrosilation reaction;

30

35

R^2 and R^3 represent aryl radicals that are σ -bonded to platinum and are independently selected from monocyclic and polycyclic aryl radicals preferably containing 6 to 18 carbon atoms, said aryl radicals being

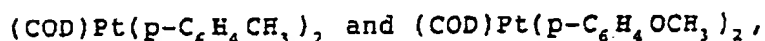
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either unsubstituted or substituted with one or more groups that are inert in a hydrosilation reaction;

- 5 R^4 and R^5 each independently represents hydrogen, or an alkenyl radical preferably containing 2 to 6 carbon atoms in a straight or branched chain, or a
- 10 cycloalkenyl radical containing 5 or 6 ring carbon atoms, the unsaturated bond of the alkenyl or cycloalkenyl radical being in the 2- or 3-position with respect to the σ -bonded position; and
- 15 a represents zero or one, being zero only when both R^4 and R^5 are said alkenyl radicals and being one when either R^4 or R^5 is not said alkenyl radical.

11. The process of Claim 10, wherein the
- 20 platinum complex is selected from the group consisting of:



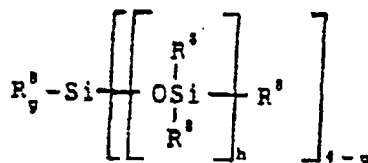
- 25 in which (COD) represents the (η^4 -1,5-cyclooctadiene) group.

12. The process of Claim 1, wherein the composition comprises from about 0.1 to about 10.0
- 30 equivalent weights of the compound having silicon-bonded hydrogen per equivalent weight of the compound having aliphatic unsaturation, and, per 1,000,000 parts by weight of the total composition, from about 5 to about
- 35 1,000 parts by weight of the platinum catalyst, and from about 50 to about 50,000 parts by weight of the sensitizer.

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13. The process of Claim 1, wherein the compound containing aliphatic unsaturation is a polyorganosiloxane having the general formula:



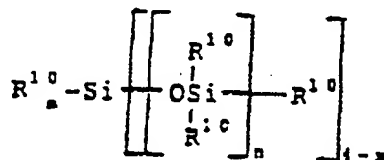
10 herein

each R^h independently represents a member selected from the group consisting of non-halogenated or halogenated ethylenically-unsaturated groups, non-halogenated or halogenated alkyl groups, non-halogenated or halogenated cycloalkyl groups, and the phenyl group, provided that at least 70% of all R^h groups are methyl groups, but no more than 10% of all R^h groups are vinyl groups or other alkenyl groups, further provided that at least two of the R^h groups are vinyl groups or other alkenyl groups,

h represents a number having a value from 1 to about 3,000, and

g represents 0, 1, 2, or 3.

14. The process of Claim 1, wherein the compound containing silicon-bonded hydrogen is a polyorganohydrosiloxane having the general formula:



35 wherein

each R^{10} independently represents a member selected from the group consisting of alkyl groups, cycloalkyl groups, the phenyl group, and

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- hydrogen, provided that at least two but no more than one-half of all the R^{10} groups in the siloxane are hydrogen,
- 5 m represents 0, 1, 2 or 3, and
 n represents a number having an average value from one to about 3,000.

15 15. The process of Claim 1, wherein the
10 compound having aliphatic unsaturation is one having olefinic unsaturation.

16. A radiation-curable composition comprising:
- 15 (a) a silicon compound containing at least one hydrogen atom attached to silicon per molecule, there being not more than three hydrogen atoms attached to any one silicon atom,
- 20 (b) a compound containing aliphatic unsaturation,
 (c) a (η -diolefin)(σ -aryl)platinum complex, and
 (d) a sensitizer that is capable of absorbing actinic radiation and that is capable of transferring energy to said platinum complex
- 25 when said composition is exposed to actinic radiation.

17. The composition of Claim 16, wherein said sensitizer has a triplet energy of at least

30 31 Kcal/mole.

18. The composition of Claim 16, wherein said sensitizer is a polycyclic aromatic compound.

35 19. The composition of Claim 18, wherein said polycyclic aromatic compound has from two to five rings, inclusive.

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20. The composition of Claim 19, wherein said polycyclic aromatic compound is selected from the group consisting of 9,10-dimethylantracene,
 5 9,10-dichloroanthracene, and azulene.

21. The composition of Claim 16, wherein said sensitizer is an aromatic compound containing a ketone chromophore.

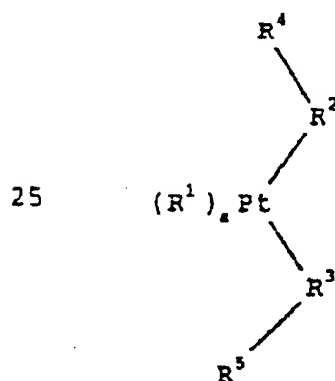
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22. The composition of Claim 21, wherein said aromatic compound is a thioxanthone.

23. The composition of Claim 22, wherein said
 15 thioxanthone is selected from the group consisting of 2-chlorothioxanthone and 2-isopropylthioxanthone.

24. The composition of Claim 16, wherein the platinum complex is represented by the formula:

20



30

wherein

35 R^1 represents an alkadiene that is π -bonded to platinum, the alkadiene being a straight or branched chain group and preferably containing 4 to 12 carbon atoms, or a carbocyclic 6- to 8-membered ring preferably containing 6 to 12 carbon atoms, the alkadiene further being either

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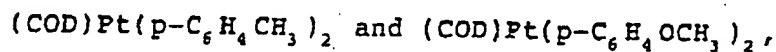
unsubstituted or substituted with one or more groups that are inert in a hydrosilation reaction;

5 R^2 and R^3 represent aryl radicals that are σ -bonded to platinum and are independently selected from monocyclic and polycyclic aryl radicals preferably containing 6 to 18 carbon atoms, said aryl radicals being
10 either unsubstituted or substituted with one or more groups that are inert in a hydrosilation reaction;

R^4 and R^5 each independently represents
15 hydrogen, or an alkenyl radical preferably containing 2 to 6 carbon atoms in a straight or branched chain, or a cycloalkenyl radical containing 5 or 6 ring carbon atoms, the unsaturated bond of the alkenyl or cycloalkenyl radical being in
20 the 2- or 3-position with respect to the σ -bonded position; and

a represents zero or one, being zero only when both R^4 and R^5 are said alkenyl radicals and being one when either R^4 or R^5 is not
25 said alkenyl radical.

25. The composition of Claim 24, wherein the platinum complex is selected from the group consisting of:



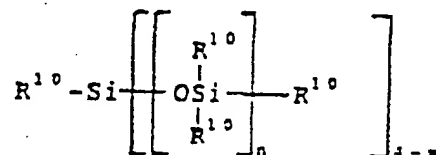
in which (COD) represents the (η^4 -1,5-cyclooctadiene) group.

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26. The composition of Claim 16, said composition comprising from about 0.1 to about 10.0 equivalent weights of the compound having silicon-bonded hydrogen per equivalent weight of the compound having aliphatic unsaturation, and per 1,000,000 parts by weight of the total composition, from about 5 to about 1,000 parts by weight of the platinum complex and from about 50 to about 50,000 parts by weight of the sensitizer.

27. A radiation-curable composition comprising:

(a) a polyorganohydrosiloxane having the general formula:



wherein

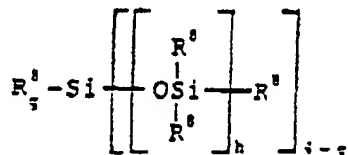
each R^{10} independently represents a member selected from the group consisting of alkyl groups, cycloalkyl groups, the phenyl group, and hydrogen, provided that at least two but no more than one-half of all the R^{10} groups in the siloxane are hydrogen,

m represents 0, 1, 2 or 3, and

n represents a number having an average value from one to

about 3,000,

(b) a polyorganosiloxane having the general formula:



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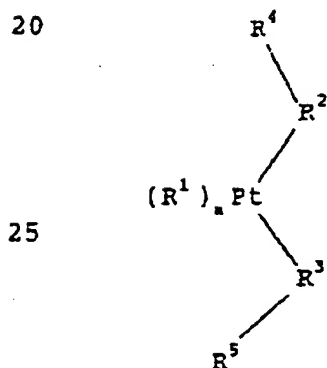
wherein

each R^8 independently represents a member selected from the group consisting of non-halogenated or halogenated ethylenically unsaturated groups, non-halogenated or halogenated alkyl groups, non-halogenated or halogenated cycloalkyl groups, and the phenyl group, provided that at least 70% of all R^8 groups are methyl groups, but no more than 10% of all R^8 groups are vinyl groups or other alkenyl groups, further provided that at least two of the R^8 groups are vinyl groups or other alkenyl groups,

h represents a number having a value from 1 to about 3,000, and

g represents 0, 1, 2, or 3,

(c) a platinum complex represented by the formula:



wherein

R^1 represents an alkadiene that is π -bonded to platinum, the alkadiene being a straight or branched chain group and preferably containing 4 to 12 carbon atoms, or a carbocyclic 6- to 8-membered ring preferably containing 6 to 12 carbon atoms, the alkadiene further being either unsubstituted or substituted with one or

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more groups that are inert in a hydrosilation reaction;

5 R^2 and R^3 represent aryl radicals that are σ -bonded to platinum and are independently selected from monocyclic and polycyclic aryl radicals preferably containing 6 to 18 carbon atoms, said aryl radicals being either unsubstituted or substituted with
10 one or more groups that are inert in a hydrosilation reaction;

R^4 and R^5 each independently represents hydrogen, or an alkenyl radical preferably containing 2 to 6 carbon atoms in a
15 straight or branched chain, or a cycloalkenyl radical containing 5 or 6 ring carbon atoms, the unsaturated bond of the alkenyl or cycloalkenyl radical being in the 2- or 3-position with respect to the σ -bonded position; and
20

a represents zero or one, being zero only when both R^4 and R^5 are said alkenyl radicals and being one when either R^4 or R^5 is not said alkenyl radical,

25 (d) a sensitizer that is capable of absorbing actinic radiation and that is capable of transferring energy to said platinum complex when said composition is exposed to actinic radiation.

30 28. A substrate bearing on at least one major surface a layer prepared by applying the composition of Claim 16 to said surface and then exposing said composition to actinic radiation.

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29. A pressure-sensitive adhesive tape comprising a backing bearing on one major surface thereof a layer of normally tacky and pressure-sensitive adhesive, and bearing on the other major surface thereof a release surface prepared by applying on said other major surface the composition of Claim 16 and then exposing said composition to actinic radiation.

30. An adhesive tape comprising a backing bearing on at least one major surface thereof a silicone adhesive prepared by applying on said at least one major surface the composition of Claim 16 and then exposing said composition to actinic radiation.

31. The tape of Claim 30, wherein said silicone adhesive is a pressure-sensitive adhesive.

32. A gasket prepared by exposing the composition of Claim 16 to actinic radiation.

33. An adhesive prepared by exposing the composition of Claim 16 to actinic radiation.

34. A conformal coating prepared by exposing the composition of Claim 16 to actinic radiation.

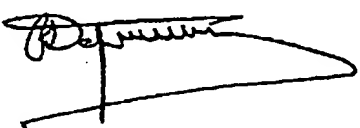
35. A dental impression prepared by exposing the composition of Claim 16 to actinic radiation.

INTERNATIONAL SEARCH REPORT

PCT/US 91/08441

International Application No.

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08L83/07; C08G77/38; C08K5/56; C08K5/00 C07F7/08		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08L ; C08G ; C08K ; C07F	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X, D	EP, A, O 122 008 (MINNESOTA MINING AND MANUFACTURING COMPANY) 17 October 1984 cited in the application see claims 1-13 see page 4, line 14 - page 6, line 4 see page 16, line 9 - line 16 ---	1-35
X, D	EP, A, O 358 452 (MINNESOTA MINING AND MANUFACTURING COMPANY) 14 March 1990 see claims 1-29 see page 4, line 19 - page 5, line 10 ---	1-9
X, D	EP, A, O 146 307 (MINNESOTA MINING AND MANUFACTURING COMPANY) 26 June 1985 see claims 1, 2, 4, 5-16 see page 8, line 12 - page 9, line 36 see page 16, line 12, paragraph 19 ---	1-9
-/-		
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
19 FEBRUARY 1992	27. 02. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	DEPIJPER R.D.C.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category*	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A, D	EP, A, 0 011 714 (WACKER-CHEMIE G.M.B.H.) 11 June 1980 see claims 1,2 --- 	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9108441
SA 54189**

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The members are as contained in the European Patent Office EDP file as
The European Patent Office is in no way liable for those particulars which are merely given for the purpose of information. 19/02/92

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